

11/11/02
Composition which cures using visible light and its use

The invention relates to a composition which cures using visible light and its use in a shaping process.

Plastics which cure using visible light are known from European application 0 897 710 for use in dental products.

In addition, it is known to use plastics which cure using UV light in the shaping process of stereolithography.

The object of the invention is to indicate an improved plastic which cures in visible light and which is suitable particularly for shaping processes, such as microphotosolidification, for other rapid-prototyping processes, such as stereolithography or for the production of dental products.

This object is achieved by a composition according to claim 1, a use of the composition according to one of claims 17 to 20, a process according to one of claims 21 to 24 or an object according to claim 25.

Further developments of the invention are indicated in the sub-claims.

Further features and advantages can be seen from the following description of exemplary embodiments of the invention using the figure.

Figure 1 shows a device for the process of producing a three-dimensional object by means of microphotosolidification from a plastic of the invention which cures under the action of visible light.

Below, the composition of the invention is illustrated using an exemplary embodiment of its use, namely of the production of a three-dimensional object by means of microphotosolidification.

As can be seen from Figure 1, the device has a container 1, which is open at its upper side, having an upper rim 2. A carrier 3 for supporting an object 4 to be formed having an essentially flat and horizontally aligned building platform 5, which may be displaced up and down and positioned in the container 1 by means of a height-adjustment device, is arranged in the container. The entire container 1 is filled up to a level below the upper rim 2 with the composition of the invention in the form of a liquid plastic 6 which cures in visible light. A flat transparent plate 7 made from a material which is transparent to visible light is provided at a predetermined distance below the upper rim 2 of the container 1, such that it is immersed by a predetermined amount into the liquid plastic 6 while the container 1 is filled with the liquid plastic 6.

An illuminating device 8 having a light source 9, such as a halogen, deuterium, plasma, mercury-vapour lamp or a laser, is provided above the container 1 for producing visible light in a wavelength range of, for example 350 to 700 nm. The illuminating device 8 also has a projection optical system and a mask-producing device and a mask 10 for the selective illumination of a particular layer of the three-dimensional object 4 to be formed in a corresponding cross-section. A diaphragm 11 which can be pivoted into the ray path is provided between the illuminating device 8 and the container 1. Furthermore, a control 12 is provided, which is designed so that it controls the diaphragm 11, the mask-producing device 10 and the height-adjustment device of the carrier 3 or the building platform as a function of predetermined object data.

In the process for producing the three-dimensional object 4, the container 1 is filled with the liquid plastic 6 which cures using visible light, and the building platform 5 is displaced by the associated height-adjustment device such that a layer of liquid plastic 6

which cures using visible light in a predetermined layer thickness is formed between the upper side of the building platform 5 and the lower side of the transparent plate 7.

Illumination of the plastic layer then takes place in a cross-section corresponding to the three-dimensional object 4 to be formed. The building platform 5 is then displaced vertically downwards in order to form the next layer of liquid light-curable plastic 6 between the upper surface of the object 4 and the transparent plate 7. These steps are repeated successively until the object 4 with its entire height is formed. The mask-producing device 10 is thus actuated via control 12 such that illumination takes place at a light intensity which suffices to penetrate the layer of liquid plastic 6 between the upper surface of the object 4 and the transparent plate 7 and to join it with the underlying already solidified layer of the object 4.

The plastic 6 consists of a composition which cures using or in visible light having
(a) 2-99 wt.% of at least one compound which contains acrylate and/or methacrylate groups, and/or vinyl and/or epoxy and/or oxetane groups and/or acryl-epoxy oligomer groups and/or methacryl-epoxy oligomer groups, and/or at least one resin composition based on polymerisable polysiloxanes, in particular ormocers,
(b) 0.01-7 wt.% of at least one initiator,
(c) 0-5 wt.% of at least one co-initiator,
(d) 0-85 wt.% of modifiers, such as fillers, dyestuffs, pigments, flow improvers, thixotropic agents, polymeric thickeners, oxidising additives, stabilisers and retardants.

The compound or the compounds of constituent (a) of the composition, which contain acrylate and/or methacrylate groups, cure in visible light by free-radical polymerisation. The following crosslinkable and non-crosslinkable monomers are particularly suitable: aliphatic diurethane methacrylate, tetra-ethoxylated bisphenol A dimethacrylate, aliphatic urethane methacrylate, 2-hydroxyethyl acetate, hydroxypropyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, iso-propyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methacrylic acid esters having an ester group of

1 to 13 C atoms, isobornyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, ethyl triglycol methacrylate, tetrahydrofurfuryl methacrylate, hydroxyalkyl methacrylates having an alkyl group of 1 to 4 C atoms, such as for example 2-hydroxyethyl methacrylate, alkoxyethyl methacrylate having an alkoxy group of 1 to 4 C atoms, allyl methacrylate, ethylene glycol dimethacrylate, diethyl glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylates, 1,3-butane diol dimethacrylate, 1,4-butane diol dimethacrylate, 1,6-hexane diol dimethacrylate, 1,12-dodecane diol dimethacrylate, glycerin-1,3-dimethacrylate, diurethane dimethacrylate, trimethylol propane trimethylacrylate.

The compound or compounds of constituent (a) containing epoxy and/or an oxetane groups cure under the action of visible light by cationic polymerisation. Examples of these are aliphatic or aromatic epoxides, cycloaliphatic epoxides or oxetanes, such as 1,3,5,7-tetrakis-(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7-tetramethylcyclotetrasiloxane, 1,10-decanediylbis(oxymethylene)bis(3-ethyloxetane), 1,3,5,7,9-pentakis(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7,9-pentamethylcyclopentasiloxane, vinylcyclohexene oxide, vinylcyclohexene dioxide, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate, bis(2,3-epoxycyclopentyl)ether; 3,4-epoxy-6-methylcyclohexylmethyl adipate, 3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy(cyclohexane-metadioxane), 1,4-butane-diylbis(oxymethylene) bis (3-ethyloxetane), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 1,1,3,3-tetramethyl-1,3-bis(2,1-ethanediyl-3,4-epoxycyclohexyl)disiloxane and/or bis-(3,4-epoxycyclohexylmethyl) adipate, 3,4-epoxycyclohexylmethyl-3'-4'-epoxycyclohexane carboxylate.

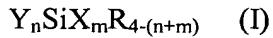
The compound or compounds of constituent (a) of the composition containing vinyl groups, such as for example monovinyl ether, divinyl ether, hydroxyvinyl ether, aminovinyl ether, trivinyl ether, cure by light in free-radical and cationic manner (mostly

cationic). Examples of these are triethylene glycol divinyl ether, 4-hydroxybutylvinyl ether, propenyl ether from propylene carbonate, dodecyl-vinyl ether, triethylene glycol divinyl ether, alkyl-vinyl ether having an alkyl group of 2 to 18 C atoms, ethylene glycol-monovinyl ether, diethylene glycol divinyl ether, butane diol-monovinyl ether, butane diol-divinyl ether, hexane diol-divinyl ether, ethylene glycol-butyl-vinyl ether, cyclohexane-dimethanol-monovinyl ether and cyclohexane-dimethanol-divinyl ether, 2-ethyl-hexyl-vinyl ether, poly-THF-divinyl ether, cyclohexyl-vinyl ether, tert.-butyl-vinyl ether, tert.-amyl-vinyl ether, ethylene glycol-divinyl ether, diethylene glycol-monovinyl ether, hexane diol-monovinyl ether, tetraethylene glycol-divinyl ether, trimethylol-propane-trivinyl ether, aminopropylvinyl ether, 2-diethylaminoethyl-vinyl ether.

The compound or compounds of constituent (a), which contains or contain acryl-epoxy oligomer groups and/or methacryl-epoxy oligomer groups, polymerise under the action of visible light both cationically and by free-radical in the form of so-called dual hardening. The combination of one or more of the above-mentioned cationically polymerising compounds with one or more of the above-mentioned free-radical polymerising compounds likewise leads to dual hardening.

The resin composition or resin compositions based on polymerisable polysiloxanes, in particular ormocers, contains or contain, for example compounds as described in the patents German Patentschrift 4 133 494 or German Offenlegungsschrift 3 903 407. It is for example a resin composition based on polymerisable polysiloxanes which can be hardened photochemically or thermally in the presence of initiators or one which is self-hardening, which can be obtained by hydrolytic condensation of one or more hydrolytically condensable compounds of silicon and optionally other elements from the group B, Ba, Ti, Zr, Al, Sn, the transition metals, the lanthanides and the actinides, and/or pre-condensates derived from the above-mentioned compounds, optionally in the presence of a catalyst and/or a solvent, by the action of water or moisture, wherein 1 to

100 mole %, based on the monomeric compounds, are selected from silanes of the general formula (I),



in which the radicals X, Y and R are the same or different and have the following meaning:

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl

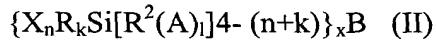
X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxycarbonyl, or NR'₂ where

R' = hydrogen, alkyl or aryl,

Y = a substituent, which contains a substituted or unsubstituted 1,4,6-trioxyaspiro-[4,4]-nonane radical,

n = 1, 2 or 3, m = 1, 2 or 3, where n+m ≤ 4,

and/or from silanes of the general formula (II),



in which the radicals A, R, R₂ and X are the same or different and have the following meaning:

A = O, S, PR', POR', NHC(O)O or NHC(O)NR', where R' = hydrogen, alkyl or aryl,

B = straight-chain or branched organic radical, which is derived from a compound B' having at least one (for l = 1 and A = NHC(O)O or NHC(O)NR') or at least two C=C double bonds and 5 to 50 carbon atoms, where R' = hydrogen, alkyl or aryl,

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl,

R² = alkylene, arylene or alkylene-arylene,

X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxycarbonyl or NR'₂, where

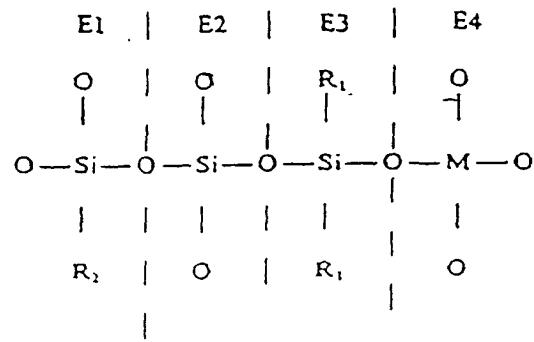
R' = hydrogen, alkyl or aryl,

$n = 1, 2, \text{ or } 3, k = 0, 1 \text{ or } 2, l = 0 \text{ or } 1,$

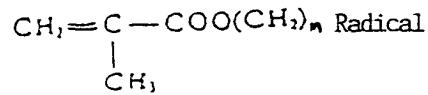
$x = \text{a whole number, the maximum value of which corresponds to the number of double bonds in the compound } B' \text{ minus } 1, \text{ or is equal to the number of double bonds in the compound } B', \text{ when } l = 1 \text{ and } A \text{ represents } \text{NHC(O)} \text{ or } \text{NHC(O)NR}',$

optionally containing fillers and/or copolymerisable monomers.

In a further example, a compound composed of the structural element E 2 and at least one of the structural elements E 1 and/or E 3 and/or E 4 of the general formula



wherein R_1 denotes a methyl, ethyl, n-propyl, isopropyl or an optionally $CH_3-C_3H_7$ -substituted phenyl radical, R_2 denotes a $CH_2=CH$, $CH_2=CHCOO(CH_2)_n$ or



or R1, n denotes 0, 1, 2 or 3, and M denotes titanium or zirconium, is present in the resin composition. The molar ratio of the structural element E 2 to the structural elements E 1 and/or E 3 and/or E 4 thus lies in each case between 50:1 and 10:1 or the molar ratio of the structural elements E2:E1:E3:E4 lies at about 25:1:1:1. Polymerisation of the polysiloxanes takes place by free radical and/or cationically.

As constituent (b) of the composition, in the case of the free-radical hardening, one or more of the following compounds initiating polymerisation is or are provided: phosphine oxides, acylphosphine oxides, diphenyl-2,4,6-trimethylbenzoylphosphine oxide; benzoin ethers, such as benzoin or the benzoin-alkyl ethers; benzil ketals, such as benzil dialkyl ketal; α -hydroxyketones; α -aminoketones; acetophenones, such as α -hydroxyacetophenones, dialkoxyacetophenones, α -aminoacetophenones, benzophenones; thioxanthones, such as i-propyl thioxanthone; α -dicarbonyl compounds, such as camphor-quinone; bisimidazoles; metallocenes, such as titanocenes and ferrocenes; aryl-tert.-butyl peresters; xanthenes; fluorenes; and/or fluorones, such as 5,7-diido-3-butoxy-6-fluorones.

In the case of cationic hardening, constituent (b) of the composition contains as initiator one or more of the following compounds: aryl diazonium salts, aryl sulphonium salts, aryl iodonium salts, ferrocenium salts and/or phenylphosphonium-benzophenone salts.

In the case of a dual-hardening compound or compound combination of constituent (a), a combination of one or more of the above-mentioned compounds initiating free-radical polymerisation with one or more of the above-mentioned compounds initiating cationic polymerisation, is provided as constituent (b). Hence, the dual-hardening composition and/or required properties may be adjusted.

Constituent (c) may contain as co-initiators for free-radical hardening, one or more of the following compounds: tertiary amines, preferably N,N-dimethyl-p-toluidine, N,N-

dihydroxyethyl-p-toluidine, N,N-dialkyl-dialkyylaniline and other structure-related amines, preferably in combination with initiators, such as benzophenones and α -dicarbonyl compounds, such as camphor-quinone; diaryl iodonium compounds, preferably in combination with the fluorone initiators; borates, such as for example butyrylcholine-triphenylbutyl borate and other structure-related borates; organic phosphites; thioxanthones as sensitisers for the α -aminoacetophenone initiators.

As co-initiators of constituent (c), one or more of the following compounds may be provided for cationic hardening: xanthenes; fluorenes; fluorones; α -dicarbonyl compounds, such as for example camphor-quinone as sensitiser for the diaryl iodonium initiators.

In the case of a dual-hardening composition, a combination of one or more of the above-mentioned co-initiators for free-radical polymerisation with one or more of the above-mentioned co-initiators for cationic polymerisation, such as for example a combination of fluorones, diaryl iodonium salts, tertiary amines and/or borates, may be provided together with corresponding initiators of constituent (b) as constituent (c).

Constituent (d) may contain at least one modifier, for example contain at least one pigment and/or a dyestuff, such as for example anthraquinone, preferably in a quantity of 0-3 wt.%. The dyestuff/ pigment is precisely matched to the light source used, or its emission spectrum. This means, if a different light source is used, if possible the dyestuff/pigment must also be changed.

At least one of the following materials may be provided as suitable filler of constituent (d) of the composition: silicon dioxide, such as pyrogenic silicon dioxide and/or amorphous silicic acid, aluminium oxide, ceramic, quartz, ground glasses, fragment polymers, silica gels and minerals. To improve bonding with the remaining constituents of the composition, the filler may be pretreated with a silane, such as for example 3-

methacryloyloxypropyl trimethoxysilane. The grain sizes of the inorganic fillers are conventionally 0.01-100 µm, preferably 0.01-20 µm.

Furthermore, fibres and fabrics, such as for example glass fibres, carbon fibres, textile fibres, metal fibres, may be embedded as fillers. This includes fibres and fabrics individually or in tape, mat, hose or cord form or a bundle of continuous fibres. It is thus not important whether the filler is present in the plastic from the start or whether the polymerisation process is interrupted, in order to insert, for example a glass-fibre mat. If the plastic formulation contains the filler, a liquid, semi-solid to solid paste is obtained regardless of the filler content. Semi-solid or solid pastes are brought to the defined layer thickness (for example 10 – 150 µm), deviating from Figure 1, by a roller system. The introduction of fillers makes possible a plurality of further areas of use, such as for example dental and otoplastic applications and applications in face and bone surgery.

In addition, constituent (d) of the composition may contain stabilisers, such as hydroquinone, hydroquinone monomethyl ether, pyrocatechol and/or 2,6-di-tert.-butyl-4-methylphenol, preferably in a quantity of 0-5 wt.%.

Examples of a composition of the invention are mentioned in the following table.

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Constituent	Designation	Example 1 Wt.%	Example 2 Wt.%	Example 3 Wt.%	Preferred Range Wt.%
(a)	1,4-Butane diol dimethacrylate	29.0	13	29.5	20 – 40
(a)	Aliphatic diurethane methacrylate	35.1	20	35	10 – 50
(a)	Tetra-ethoxylated bisphenol A dimethacrylate	-	37.7	-	15 – 45
(a)	Aliphatic urethane methacrylate	30.0	25	30	15 – 45
(d)	Anthraquinone dyestuff	1.0	0.3	0.6	0.1 – 1.5
(c)	Tertiary amine	2.0	2.0	2.0	0.3 – 4
(b)	Acylphosphine oxide	1.0	0.1	1.0	0.05 – 1.0
(b)	Fluorone initiator	0.5	0.5	0.5	0.05 – 1.5
(c)	Iodonium salt	1.4	1.4	1.4	0.1 – 5

When using the composition indicated in Example 1 as the plastic 6 in the process described above, curing depths of 115-211 µm may be obtained for illumination times of 4-12 seconds. Hence, layer thicknesses of 55 – 105 µm are produced with the above-mentioned arrangement. Layer thicknesses of 1 – 250 µm are achieved by varying the plastic composition. A halogen lamp is used in the process.

The composition is produced by the following essential steps: initially prescribed quantities of initiators, co-initiators, dyestuffs, pigments and stabilisers are dissolved in a slightly viscous part of constituent (a) of the composition, such as for example in the

monomer ethyl methacrylate or butane diol dimethacrylate, wherein the resulting mixture are stirred depending on solubility capacity of the constituents used for between 1-36 hours at 20-80°C. The resulting solution is then mixed with the rest of constituent (a) of the composition for 10-60 minutes. Optionally one or more fillers are then added to the resulting solution in small portions and mixed intensively after every addition.

During production, physical properties, such as the hardness or depth of hardness of a layer, the modulus of elasticity, the colour, the layer thickness and the durability of the object to be formed may be influenced by the selection of type and quantity of the fillers, pigments, dyestuffs and stabilisers of the composition and adjusted as required. Furthermore, the initiators and/or co-initiators may be used in different combinations in order to vary them according to the type of shaping process, the light source thus used and the required physical properties of the object to be formed therewith.

In the case of a dual-hardening composition, the accuracy of fit of the object to be formed may be improved, since, for example compared to a composition hardening purely by free radical, the polymerisation shrinkage and the interfering influence of an oxygen inhibition layer is reduced.

By precise matching of the composition of the plastic used in the shaping process, the light source used, the mask, the type and/or the intensity of the radiated light, the thickness of a layer to be hardened in the shaping process may be adjusted to the required thickness. In addition, the layer thickness and the depth of hardness over the polymerisation depth and the polymerisation time may be influenced by adding suitable dyestuffs and/or by varying the concentrations of the initiators and/or co-initiators or by the selection and combination of one or more initiators and/or one or more co-initiators.

The plastic of the above-mentioned composition may be used in the process described above for forming a three-dimensional object, that is during microphotosolidification, and

also for other rapid-prototyping processes, for example during laser sintering or in stereolithography.

The use of the composition of the invention is not restricted to microphotosolidification or to rapid-prototyping processes. The composition of the invention can rather also be used for other shaping processes, such as for example during film-casting of plastics, in the production of plastic sintered parts or in microstructuring, such as for example during photolithography in semi-conductor technology. In addition, the composition of the invention can be used in the dental field, the field of face and bone surgery and the otoplastic field for producing inlays, onlays, tooth fillings, attachments, crowns, bridges, artificial teeth, crown teeth, tooth prostheses, tooth implants, face implants, bone implants and hearing aids (otoplastics). Consequently, both models and also individually made single products or mass-produced sales products may be produced using the composition of the invention.

A specific use of the composition of the invention is given in dental technology in a process for producing plastic inlays. In the process, initially an image of a cavity of a tooth to be filled is made in known manner using a camera and a computer model of the inlay to be inserted in the cavity is produced. The computer model is then divided into flat layers by means of software, wherein the layer data thus produced supplies the control of a microphotosolidification plant described above, where the inlay is built up layer by layer corresponding to the layer data. Inlays can thus be produced in precise manner by good resolution during the process of microphotosolidification. In the process of the invention, a plastic as described above is used, which is tooth-coloured by addition of appropriate dyestuffs/pigments.

Alternatively, the inlay may also be produced by using a plastic which is paste-like due to a filler of constituent (d), wherein each layer is produced by rolling-out the paste-like material. Particular stiffness of the inlay produced can be achieved if glass-fibre

constituents are added to the plastic composition to be cured. Alternatively, after curing one or more plastic layers, a glass-fibre mat may also be laid therebetween.